

Vibration-induced first-order Stark effect in tetrahedral molecules: SiH₄ and SiF₄

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The vibration-induced permanent dipole moments in SiH₄ and in SiF₄ have been determined by measuring the first-order Stark effect on the infrared vibration-rotation lines in the triply degenerate ν_4 and ν_3 fundamental bands, respectively. Microwave modulation sidebands on CO₂ laser lines were generated with sufficient power and spectral purity to be used as the frequency-tunable infrared source for the sub-Doppler saturation Lamb dip measurements. Theory is also presented for calculating the dipole moment matrix elements in the excited vibrational state. From the observed Stark splittings, the vibration-induced permanent dipole moment P has been determined to be $1.46(5) \times 10^{-2}$ D for SiH₄ in the $\nu_4 = 1$ state, and $4.21(12) \times 10^{-2}$ D for SiF₄ in the $\nu_3 = 1$ state. In addition, Watson's coefficient for the rotation-induced permanent dipole moment θ_z^{xy} has been determined to be $2.97(19) \times 10^{-5}$ D in SiH₄ ($\nu_4 = 1$).

I. INTRODUCTION

The existence of a vibration-induced permanent dipole moment was originally proposed by Mizushima and Venkateswarlu,¹ who considered molecules with D_{2d} or T_d symmetry, in a doubly or triply degenerate excited vibrational state, respectively. Mills, Watson, and Smith² further developed the theory to include molecules of many other symmetries. Such vibration-induced permanent dipole moments can give rise to Stark effects³⁻⁵ and normally forbidden rotational transitions.⁶⁻¹¹ In addition, experimentalists have confirmed the existence of such a dipole moment by molecular beam electric deflection techniques¹² and level crossing experiments.¹³

Watson has shown that, in the case of a nonpolar molecule, only those rovibrational levels with E symmetry can exhibit a first-order Stark effect.¹⁴ This behavior can obviously be utilized for spectroscopic purposes, e.g., Stark modulation for phase-sensitive detection. Also, the vibration-induced permanent dipole moment is related to the cubic anharmonic force constants and the second derivative of the dipole moment² and hence can provide information on these parameters. However, a dipole moment induced by vibration should be on the order of κ^2 smaller than a typical permanent dipole moment (κ is the Born-Oppenheimer constant), or 10^{-2} D. At moderate electric fields, splittings are expected to be a few MHz only, well within the Doppler linewidth if measured in the infrared, therefore, a sub-Doppler technique is required.

We have used Lamb dip spectroscopy^{15,16} to measure infrared transitions between E rovibrational levels in the fundamental band of the triply degenerate vibrations (ν_3 or ν_4) in SiH₄ and SiF₄. Simultaneously, we applied a dc elec-

tric field to Stark plates in the cell, and from the resultant Stark splittings, determined the vibration-induced permanent dipole moment in these two molecules.

II. EXPERIMENTAL

The source and cell arrangement are described in detail elsewhere¹⁷ and will not be elaborated on here. Briefly, tunable infrared radiation is generated by mixing CO₂ laser radiation (ν_l) and microwave radiation ($\nu_{mw} = 12-18$ GHz) in a nonlinear CdTe crystal. The resulting sidebands, at frequencies $\nu_{SB} = \nu_l \pm \nu_{mw}$, are easily frequency tuned by tuning the microwave; they are of high enough spectral purity (< 40 kHz) and sufficiently powerful (~ 2 mW) for saturation Lamb dip spectroscopy.

Since the earlier work was published, a multiple reflection White cell has been employed. This requires that the two counterpropagating beams be exactly collinear, necessitating the use of a Brewster window and Fresnel rhomb combination, as described in Ref. 18. The polarization of the sideband in the sample cell, is, in this case, circular. Stark plates spaced 1 cm apart were employed, and field homogeneity was determined to be better than 1% by measuring the linewidths of numerous CH₃F lines. Due to the circular polarization of the incident beam, pertinent selection rules are $\Delta M = 0$ and $\Delta M = \pm 1$.

Transition frequencies for the ν_3 band of SiF₄ were calculated from the molecular constants of Patterson *et al.*¹⁹ and those for the ν_4 band of SiH₄ were taken from Refs. 20 and 21. Typical pressures were 1 and 10 mTorr for SiH₄ and SiF₄, respectively.

III. THEORY

When a tetrahedral molecule is in the $\nu = 1$ state of a triply degenerate (F_2) vibration, vibrational angular momentum l couples with the rotational angular momentum R , to form the resultant angular momentum J ($= R - l$). This

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Coriolis coupling causes a first-order splitting of the $\nu = 1$ state into three levels, for $R = J + 1, J,$ and $J - 1$. In the $\nu = 0$ state, $l = 0$ and there is no splitting from Coriolis interactions. However, centrifugal distortion in the ground state (and excited state) and vibration-rotation interaction in the $\nu = 1$ state cause a further splitting of the levels into a series of lines with the symmetry labels of the tetrahedral point group (Fig. 1). Hecht has shown that this tetrahedral fine structure results from a fourth rank spherical tensor operator, in both the ground and excited states of a triply degenerate vibration.²² In Hecht's notation, the centrifugal distortion operator is O_{pppp} and the vibration-rotation interaction operator is O_{pp33} . He has also shown that because the pertinent operator in both states is a fourth rank spherical tensor operator, although the magnitude of the splittings in the two states may be different, the pattern is identical (Fig. 1) and depends solely on R ($= J$ in the $\nu = 0$ state). The ramifications of this relationship will be discussed later.

We will be concentrating on transitions between levels with E symmetry since only these levels have double parity and hence exhibit a first order Stark effect. In the presence of a dc electric field, these levels are shifted by an amount:

$$\Delta E = C(R, \kappa)^\nu \cdot M_J P E, \tag{1}$$

where κ is the symmetry label of the levels (E only, in this

case), $C(R, \kappa)^\nu$ is a constant for a particular value of R and κ , M_J is the space-fixed z component of total angular momentum J , and E is the magnitude of the electric field. The value of $C(R, \kappa)^\nu$ is different for each component of the Coriolis sublevel, as discussed later. P is the vibration-induced dipole moment (2):

$$P = \langle v_{i\beta} = 1, v_{i\alpha} = v_{i\gamma} = 0 | (\mu_\alpha)_{\text{eff}} | v_{i\gamma} = 1, v_{i\alpha} = v_{i\beta} = 0 \rangle = (\hbar/2\lambda_i^{1/2}) \left[\left(\frac{\partial^2 \mu_z}{\partial Q_{i_x} \partial Q_{i_y}} \right)_e - \sum_{i'} \phi_{i_x, i_y, i_z} \left(\frac{\partial \mu_z}{\partial Q_{i_z}} \right)_e / \lambda_{i'} \right]. \tag{2}$$

α, β, γ ($= x, y, z$ in any order) are the S_4 axes of the tetrahedral molecule.

To determine the effective dipole moment from the Stark shift, one must first calculate the dipole moment matrix elements for a given wave function, i.e., $-\langle R, \kappa | \mu \cdot E | R, \kappa \rangle$. This calculation can be carried out in two steps: (i) Express the $|R, \kappa\rangle$ wave function as a linear combination of symmetric top basis functions $|R, K_R\rangle$, and then (ii) determine the dipole moment matrix element in this symmetric top basis.

One advantage to this approach is that the matrix elements of the tensor operator which leads to the tetrahedral fine structure are easily expressed in a symmetric top basis set.^{22,23} As mentioned earlier, the pertinent operator in both states is a fourth rank spherical tensor operator, and the splitting pattern is identical in both states. Therefore, we found it more convenient to calculate the matrix elements for the ground state centrifugal distortion Hamiltonian described by Dorney and Watson,²³ replacing J with R , and K with K_R . In addition, matrix elements were calculated using as a basis set symmetric top wave functions for a molecule with C_{3v} symmetry, that is, K_R is the component of rotational angular momentum along the C_3 molecular axis. The C_{3v} centrifugal distortion Hamiltonian was used so that not only the magnitude but also the actual sign of the Stark coefficient $C(R, \kappa)^\nu$ could be determined.²³

In addition to the wave functions $(\sum_{K_R} a_{K_R} |R, K_R\rangle)$ for a given level $|R, \kappa\rangle$, one must derive the expressions for the $-\mu \cdot E$ interaction in a $|R, K_R\rangle$ basis set. Jahn presents expressions for the wave functions which result from the Coriolis coupling of vibrational and total angular momenta to yield the rotational angular momentum R ($R = J - 1$), for $R = J + 1, J$ and $J - 1$.²⁴ With these expressions, it can be shown that the only nonzero matrix elements for the interaction

$$-\mu \cdot E = (\mu_\xi \lambda_{\xi z} + \mu_\eta \lambda_{\eta z} + \mu_\zeta \lambda_{\zeta z}) E \tag{3}$$

are

$$-\langle R, K_R | \mu \cdot E | R, K_R \rangle = K_R (3R^2 + 3R - 5K_R^2 - 1) M_J \cdot P \cdot E \cdot N(R) \tag{4}$$

and

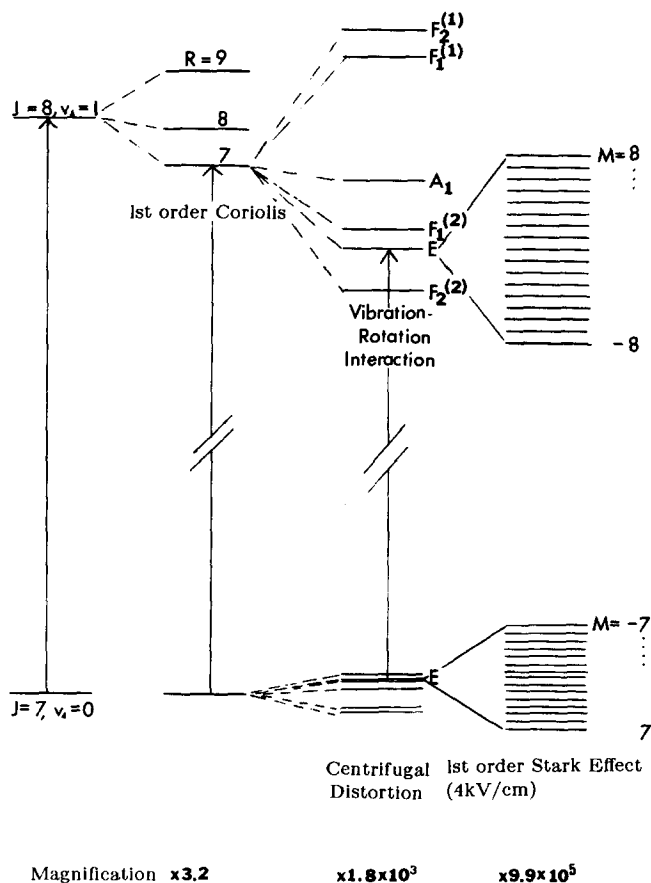


FIG. 1. Energy level diagram for the $R(7)E$ transition in the fundamental of a triply degenerate vibration of a tetrahedral molecule. Splittings due to the Coriolis interaction are magnified by a factor of ~ 3 , those due to centrifugal distortion and vibration-rotation interactions, by a factor of $\sim 2 \times 10^3$, and those due to the Stark effect, by a factor of $\sim 10^6$.

TABLE I. Centrifugal distortion Stark coefficients $C(J, \kappa, n)$.

J	n	$C(J, \kappa)$	J	n	$C(J, \kappa)$	J	n	$C(J, \kappa)$
2	1	0.173 205E + 01	29	1	0.279 276E - 02	41	1	0.101 452E - 04
4	1	-0.311 769E + 01		2	-0.376 376E + 00		2	-0.368 685E - 02
5	1	0.311 769E + 01		3	0.493 338E + 01		3	0.263 002E + 00
6	1	0.123 718E + 01		4	-0.224 783E + 02		4	-0.549 537E + 01
7	1	-0.556 731E + 01		5	0.304 013E + 02		5	0.150 792E + 02
8	1	-0.100 606E + 01	30	1	0.490 525E - 04		6	-0.370 892E + 02
	2	0.533 618E + 01		2	-0.284 973E - 01		7	0.443 553E + 02
9	1	0.242 487E + 01		3	0.141 400E + 01	42	1	0.114 655E - 06
10	1	0.431 396E + 00		4	-0.141 005E + 02		2	-0.157 721E - 03
	2	-0.836 734E + 01		5	0.232 749E + 02		3	0.253 448E - 01
11	1	-0.288 170E + 01	31	1	-0.112 696E - 02		4	-0.105 276E + 01
	2	0.839 277E + 01		2	0.182 855E + 00		5	0.776 731E + 01
12	1	-0.214 058E + 00		3	-0.500 807E + 01		6	-0.298 146E + 02
	2	0.381 139E + 01		4	0.133 683E + 02		7	0.382 605E + 02
13	1	0.128 946E + 01		5	-0.327 418E + 02	43	1	-0.385 488E - 05
	2	-0.115 676E + 02	32	1	-0.181 248E - 04		2	0.159 097E - 02
14	1	0.907 134E - 01		2	0.124 873E - 01		3	-0.134 599E + 00
	2	-0.545 262E + 01		3	-0.863 941E + 00		4	0.283 668E + 01
	3	0.120 427E + 02		4	0.679 624E + 01		5	-0.201 229E + 02
15	1	-0.846 766E + 00		5	-0.262 094E + 02		6	0.306 407E + 02
	2	0.560 991E + 01		6	0.339 045E + 02		7	-0.466 723E + 02
16	1	-0.383 918E - 01	33	1	0.448 537E - 03	44	1	-0.411 120E - 07
	2	0.246 225E + 01		2	-0.887 417E - 01		2	0.633 617E - 04
	3	-0.150 322E + 02		3	0.250 194E + 01		3	-0.116 741E - 01
17	1	0.392 238E + 00		4	-0.179 296E + 02		4	0.552 742E + 00
	2	-0.842 435E + 01		5	0.272 328E + 02		5	-0.863 763E - 01
	3	0.158 773E + 02	34	1	0.665 295E - 05		6	0.191 646E + 02
18	1	0.155 314E - 01		2	-0.537 459E - 02		7	-0.406 331E + 02
	2	-0.211 667E + 01		3	0.437 707E + 00		8	0.478 303E + 02
	3	0.802 657E + 01		4	-0.804 869E + 01	45	1	0.145 523E - 05
19	1	-0.193 820E + 00		5	0.173 362E + 02		2	-0.677 044E - 03
	2	0.386 004E + 01		6	-0.362 333E + 02		3	0.659 231E - 01
	3	-0.185 983E + 02	35	1	-0.176 451E - 03		4	-0.198 005E + 01
20	1	-0.617 550E - 02		2	0.412 421E - 01		5	0.101 435E + 02
	2	0.101 413E + 01		3	-0.175 360E + 01		6	-0.336 917E + 02
	3	-0.116 464E + 02		4	0.900 423E + 01		7	0.418 045E + 02
	4	0.196 452E + 02		5	-0.298 897E + 02	46	1	0.146 918E - 07
21	1	0.866 075E - 01		6	0.373 947E + 02		2	-0.252 148E - 04
	2	-0.418 700E + 01	36	1	-0.242 791E - 05		3	0.527 209E - 02
	3	0.111 861E + 02		2	0.227 118E - 02		4	-0.300 425E + 00
22	1	0.240 616E - 02		3	-0.228 850E + 00		5	0.437 400E + 01
	2	-0.589 013E + 00		4	0.395 319E + 01		6	-0.244 305E + 02
	3	0.550 468E + 01		5	-0.218 681E + 02		7	0.347 349E + 02
	4	-0.221 701E + 02		6	0.310 148E + 02		8	-0.501 458E + 02
23	1	-0.382 835E - 01	37	1	0.687 015E - 04	47	1	-0.546 127E - 06
	2	0.200 502E + 01		2	-0.188 389E - 01		2	0.284 470E - 03
	3	-0.151 002E + 02		3	0.909 960E + 00		3	-0.318 138E - 01
	4	0.232 998E + 02		4	-0.117 655E + 02		4	0.105 777E + 02
24	1	-0.924 479E - 03		5	0.217 652E + 02		5	-0.125 772E + 02
	2	0.281 955E + 00		6	-0.397 173E + 02		6	0.238 240E + 02
	3	-0.703 544E + 01	38	1	0.881 486E - 06		7	-0.441 552E + 02
	4	0.149 990E + 02		2	-0.945 661E - 03		8	0.513 032E + 02
25	1	0.163 043E - 01		3	0.111 866E + 00	48	1	-0.523 409E - 08
	2	-0.139 263E + 01		4	-0.323 469E + 01		2	0.994 876E - 05
	3	0.752 376E + 01		5	0.117 122E + 02		3	-0.234 420E - 02
	4	-0.257 169E + 02		6	-0.335 126E + 02		4	0.152 957E + 00
26	1	0.350 787E - 03		7	0.408 773E + 02		5	-0.347 791E + 01
	2	-0.137 797E + 00	39	1	-0.265 075E - 04		6	0.129 735E + 02
	3	0.333 263E + 01		2	0.840 437E - 02		7	-0.374 731E + 02
	4	-0.187 438E + 02		3	-0.516 306E + 00		8	0.453 241E + 02
	5	0.268 735E + 02		4	0.571 868E + 01	49	1	0.203 857E - 06
27	1	-0.681 645E - 02		5	-0.258 556E + 02		2	-0.118 173E - 03
	2	0.693 398E + 00		6	0.346 744E + 02		3	0.149 862E - 01
	3	-0.104 268E + 02	40	1	-0.318 567E - 06		4	-0.615 058E + 00
	4	0.191 428E + 02		2	0.388 477E - 03		5	0.626 548E + 01
28	1	-0.131 754E - 03		3	-0.540 866E - 01		6	-0.287 356E + 02
	2	0.631 561E - 01		4	0.168 753E + 01		7	0.386 139E + 02
	3	-0.280 593E + 01		5	-0.158 669E + 02		8	-0.536 176E + 02
	4	0.100 961E + 02		6	0.262 906E + 02			
	5	-0.292 385E + 02		7	-0.431 965E + 02			

TABLE I (continued)

<i>J</i>	<i>n</i>	<i>C(J,κ)</i>	<i>J</i>	<i>n</i>	<i>C(J,κ)</i>	<i>J</i>	<i>n</i>	<i>C(J,κ)</i>
50	1	0.185 944E - 08	58	5	0.115 059E + 01	65	2	0.463 693E - 08
	2	-0.389 504E - 05		6	-0.129 671E + 02		3	-0.233 760E - 05
	3	0.102 700E - 02		7	0.254 066E + 02		4	0.372 942E - 03
	4	-0.772 836E - 01		8	-0.483 968E + 02		5	-0.242 170E - 01
	5	0.186 367E + 01		9	0.558 134E + 02		6	0.681 089E + 00
	6	-0.170 432E + 02		1	0.288 996E - 10		7	-0.893 110E + 01
	7	0.287 207E + 02		2	-0.857 418E - 07		8	0.216 619E + 02
	8	-0.476 628E + 02		3	0.335 794E - 04		9	-0.487 250E + 02
	9	0.547 746E + 02		4	-0.401 718E - 02		10	0.566 710E + 02
51	1	-0.757 234E - 07	59	5	0.184 453E + 00	66	11	-0.709 623E + 02
	2	0.485 864E - 04		6	-0.358 532E + 01		1	0.662 998E - 10
	3	-0.694 507E - 02		7	0.139 401E + 02		2	-0.771 424E - 07
	4	0.323 407E + 00		8	-0.410 958E + 02		3	0.217 225E - 04
	5	-0.573 928E + 01		9	0.495 801E + 02		4	-0.227 633E - 02
	6	0.164 176E + 02		10	-0.640 265E + 02		5	0.103 290E + 00
	7	-0.411 710E + 02		1	-0.138 295E - 08		6	-0.215 756E + 01
	8	0.488 290E + 02		2	0.127 359E - 05		7	0.116 006E + 02
52	1	-0.658 869E - 09	60	3	-0.275 749E - 03	67	8	-0.401 307E + 02
	2	0.151 420E - 05		4	0.213 256E - 01		9	0.499 200E + 02
	3	-0.444 130E - 03		5	-0.678 981E + 00		10	-0.650 977E + 02
	4	0.378 535E - 01		6	0.661 193E + 01		11	0.721 181E + 02
	5	-0.117 298E + 01		7	-0.311 338E + 02		1	0.262 299E - 12
	6	0.846 935E + 01		8	0.421 772E + 02		2	-0.173 853E - 08
	7	-0.329 781E + 02		9	-0.581 367E + 02		3	0.947 109E - 06
	8	0.423 473E + 02		10	0.651 826E + 02		4	-0.164 892E - 03
	9	-0.570 882E + 02		1	-0.100 930E - 10		5	0.118 402E - 01
53	1	0.280 016E - 07	61	2	0.325 740E - 07	68	6	-0.386 016E + 00
	2	-0.197 895E - 04		3	-0.139 273E - 04		7	0.475 768E + 01
	3	0.316 428E - 02		4	0.184 255E - 02		8	-0.279 667E + 02
	4	-0.171 286E + 00		5	-0.960 987E - 01		9	0.407 759E + 02
	5	0.304 367E + 01		6	0.196 353E + 01		10	-0.590 197E + 02
	6	-0.217 329E + 02		7	-0.177 100E + 02		11	0.662 568E + 02
	7	0.335 053E + 02		8	0.306 191E + 02		1	-0.239 513E - 10
	8	-0.511 604E + 02		9	-0.519 569E + 02		2	0.299 557E - 07
	9	0.582 448E + 02		10	0.592 977E + 02		3	-0.914 155E - 05
54	1	0.232 905E - 09	62	1	0.503 899E - 09	69	4	0.104 955E - 02
	2	-0.584 841E - 06		2	-0.503 210E - 06		5	-0.532 191E - 01
	3	0.189 786E - 03		3	0.119 392E - 03		6	0.119 998E + 01
	4	-0.182 513E - 01		4	-0.102 780E - 01		7	-0.130 240E + 02
	5	0.631 815E + 00		5	0.365 427E + 00		8	0.265 909E + 02
	6	-0.890 537E + 01		6	-0.580 392E + 01		9	-0.524 152E + 02
	7	0.205 816E + 02		7	0.174 501E + 02		10	0.601 914E + 02
	8	-0.448 061E + 02		8	-0.449 607E + 02		11	-0.744 295E + 02
	9	0.523 244E + 02		9	0.531 362E + 02		1	-0.804 014E - 13
55	1	-0.103 120E - 07	63	10	-0.674 947E + 02	70	2	0.649 341E - 09
	2	0.799 150E - 05		1	0.333 962E - 11		3	-0.381 164E - 06
	3	-0.142 123E - 02		2	-0.123 170E - 07		4	0.721 487E - 04
	4	0.869 421E - 01		3	0.572 805E - 05		5	-0.570 545E - 02
	5	-0.210 624E + 01		4	-0.834 072E - 03		6	0.206 672E + 00
	6	0.109 966E + 02		5	0.485 890E - 01		7	-0.359 311E + 01
	7	-0.371 051E + 02		6	-0.123 987E + 01		8	0.146 516E + 02
	8	0.459 907E + 02		7	0.893 992E + 01		9	-0.443 767E + 02
	9	-0.605 577E + 02		8	-0.357 077E + 02		10	0.536 154E + 02
56	1	-0.821 419E - 10	64	9	0.461 265E + 02	71	11	-0.685 744E + 02
	2	0.244 547E - 06		10	-0.616 186E + 02		12	0.755 852E + 02
	3	-0.802 277E - 04		11	0.686 506E + 02		1	0.863 042E - 11
	4	0.862 791E - 02		1	-0.183 041E - 09		2	-0.115 740E - 07
	5	-0.352 038E + 00		2	0.197 594E - 06		3	0.381 588E - 05
	6	0.463 202E + 01		3	-0.511 678E - 04		4	-0.478 077E - 03
	7	-0.264 576E + 02		4	0.487 098E - 02		5	0.268 029E - 01
	8	0.379 939E + 02		5	-0.198 227E + 00		6	-0.714 829E + 00
	9	-0.546 511E - 02		6	0.314 937E + 01		7	0.679 028E + 01
57	10	0.617 141E + 02	65	7	-0.228 021E + 02	72	8	-0.330 577E + 02
	1	0.378 304E - 08		8	0.358 378E + 02		9	0.453 404E + 02
	2	-0.320 187E - 05		9	-0.554 958E + 02		10	-0.625 325E + 02
	3	0.629 811E - 03		10	0.627 786E + 02		11	0.697 329E + 02
	4	-0.435 724E - 01		1	-0.116 774E - 11		1	0.313 787E - 13

TABLE I (continued).

<i>J</i>	<i>n</i>	<i>C</i> (<i>J,κ</i>)
	2	-0.241 659 <i>E</i> - 09
	3	0.152 441 <i>E</i> - 06
	4	-0.312 655 <i>E</i> - 04
	5	0.270 904 <i>E</i> - 02
	6	-0.110 137 <i>E</i> + 00
	7	0.200 389 <i>E</i> + 01
	8	-0.179 440 <i>E</i> + 02
	9	0.320 462 <i>E</i> + 02
	10	-0.560 527 <i>E</i> + 02
	11	0.637 014 <i>E</i> + 02
	12	-0.778 964 <i>E</i> + 02
71	1	-0.306 874 <i>E</i> - 11
	2	0.445 093 <i>E</i> - 08
	3	-0.158 080 <i>E</i> - 05
	4	0.215 310 <i>E</i> - 03
	5	-0.133 056 <i>E</i> - 01
	6	0.391 722 <i>E</i> + 00
	7	-0.573 742 <i>E</i> + 01
	8	0.182 224 <i>E</i> + 02
	9	-0.484 515 <i>E</i> + 02
	10	0.572 495 <i>E</i> + 02
	11	-0.720 494 <i>E</i> + 02
	12	0.790 520 <i>E</i> + 02

$$\begin{aligned}
& - \langle R, K_R | \mu \cdot E | R, K_R + 3 \rangle \\
& = \{ -\sqrt{6} [(R - K_R - 2)(R - K_R - 1) \\
& \quad \times (R - K_R)(R + K_R + 1) \\
& \quad \times (R + K_R + 2)(R + K_R + 3)]^{1/2} / 6 \} \\
& \quad \times M_J \cdot P \cdot E \cdot N(R), \quad (5)
\end{aligned}$$

where

$$\begin{aligned}
N(R) &= - [R^2(R - 1)(2R - 1)]^{-1} \\
&\quad \text{for } R = J + 1, \quad (6)
\end{aligned}$$

$$N(R) = [R^2(R + 1)^2]^{-1} \quad \text{for } R = J, \quad (7)$$

and

$$\begin{aligned}
N(R) &= - [(R + 1)^2(R + 2)(2R + 3)]^{-1} \\
&\quad \text{for } R = J - 1. \quad (8)
\end{aligned}$$

P, the vibration-induced effective dipole moment, is defined in Eq. (2).

The wave functions of a given energy level $|R, \kappa\rangle$ are linear combinations of $|R, K_R\rangle$, hence, it is straightforward to calculate the shift in energy due to the interaction $-\mu \cdot E$:

$$-\langle R, \kappa | \mu \cdot E | R, \kappa \rangle = \Delta E = C(R, \kappa)^v \cdot M_J \cdot P \cdot E. \quad (9)$$

Dorney and Watson's coefficient $C(J, \kappa)$ is the analogous Stark coefficient for the rotation-induced dipole moment. Because O_{pppp} and O_{pp33} are both derived from fourth rank tensor operators, their eigenvalues are closely related. For example, if one derives the ratio g_{1J}/g_{0J} , where g_{1J} and g_{0J} are proportional to the eigenvalues of O_{pp33} and O_{pppp} , respectively,²² one finds that

$$\frac{g_{1J}}{g_{0J}} = \frac{2}{R(2R - 1)} \quad \text{for } R = J + 1, \quad (10)$$

$$\frac{g_{1J}}{g_{0J}} = \frac{2}{R(R + 1)} \quad \text{for } R = J, \quad (11)$$

and

$$\frac{g_{1J}}{g_{0J}} = \frac{2}{(R + 1)(2R + 3)} \quad \text{for } R = J - 1. \quad (12)$$

Similarly, $C(R, \kappa)^v$ and $C(J, \kappa)$, which are eigenvalues of O_{p33} and O_{ppp} , respectively (again using Hecht's notation), are also related. $C(R, \kappa)^v$ can be expressed in terms of $C(J, \kappa)$ by comparing Eq. (14) of Ref. 23 with Eqs. (4) and (5) above. One finds

$$\frac{C(R, \kappa)^v}{C(J, \kappa)} = - \frac{(R + 1)}{R(R - 1)(2R - 1)}, \quad \text{for } R = J + 1, \quad (13)$$

$$\frac{C(R, \kappa)^v}{C(J, \kappa)} = \frac{1}{R(R + 1)}, \quad \text{for } R = J, \quad (14)$$

and

$$\begin{aligned}
\frac{C(R, \kappa)^v}{C(J, \kappa)} &= - \frac{R}{(R + 1)(R + 2)(2R + 3)} \\
&\quad \text{for } R = J - 1. \quad (15)
\end{aligned}$$

The values of $C(R, \kappa)^v$ as determined by the methods described herein agree completely with the values described from Eqs. (13)–(15) and $C(J, \kappa)$. Therefore, in order to save space, the values of $C(J, \kappa = E^{(n)})$ up to $J = 71$ are presented in Table I. (The numbering of the *E* states is consistent with Dorney and Watson's convention.) These correspond to the Stark coefficient for a rotation-induced dipole moment. For the case of a vibration-induced dipole moment, for a given *R*, one must choose $C(J, \kappa)$, where $J = R$ (since $J = R$ in the ground state). Then, depending on the value of *R* with respect to *J* in the excited state, one chooses the appropriate factor from Eqs. (13)–(15).

IV. RESULTS AND DISCUSSION

Figure 2 shows a series of Stark spectra of a transition in the ν_4 band of SiH₄, as a function of electric field. Figure 3 shows the $R(7)E$ transition of SiH₄ with calculated spectrum below. As can be seen, the $\Delta M = 0$ lines are completely resolved from the $\Delta M = \pm 1$ lines. Dashed lines in the calculated stick spectrum correspond to center dips.²⁵ A transition in the ν_3 band of SiF₄ is shown in Fig. 4. Since centrifugal distortion is so small in SiF₄, there is virtually no Stark splitting in the ground vibrational state, hence $\Delta M = 0$ transitions are not resolved from $\Delta M = \pm 1$ transitions. Again, dashed lines correspond to the center dips.

A total of three vibration-rotation transitions were measured for SiH₄ and four for SiF₄, at various dc electric fields. Zero-field frequencies, calculated from the CO₂ laser line frequencies²⁶ and microwave frequencies, are presented in Tables II and III. CO₂ laser line and microwave frequencies are also indicated separately. Determination of the vibration-induced permanent dipole moment from the Stark splittings is straightforward. In the case of SiF₄, there is no Stark splitting in the ground state, hence, for a first-order effect, one would expect $2J + 1$ equally spaced peaks, where *J* refers to the excited state. Table II lists the average separa-

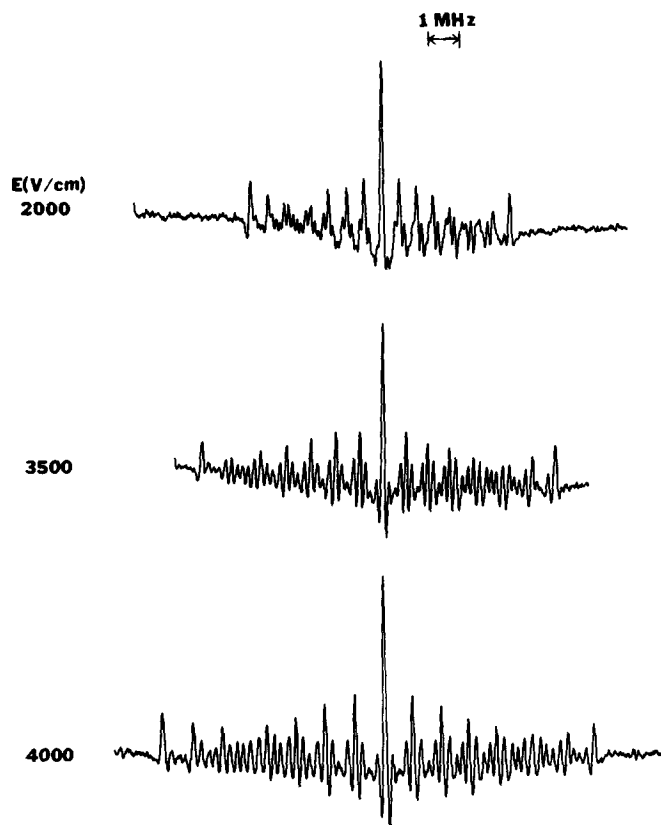


FIG. 2. The $\nu_4 \leftarrow 0 R(7)E$ transition of SiH₄, observed at various dc electric fields.

tion between minimum and maximum M components, for the four transitions measured, at various magnitudes of the dc electric field. From the magnitudes of the splittings for a given field and the values of $C(J,\kappa)$ presented in Table I and subsequently corrected by Eqs. (3)–(15), P for the ν_3 band of SiF₄ was calculated to be $4.21(12) \times 10^{-2}$ D.

The analysis of the SiH₄ Stark effect was somewhat more complicated due to the contribution of the ground state dipole moment. From a simple energy level diagram, however, one can conclude that the separation between two subsequent $\Delta M = 0$ lines in the spectrum has the following dependence:

$$\begin{aligned} \delta\omega &= \pm [C(J,\kappa) \cdot \theta_{z,4}^{x,y} + C(R,\kappa)^v \cdot P - C(J,\kappa) \cdot \theta_{z,0}^{x,y}] \cdot E \\ &= \pm [C(R,\kappa)^v \cdot P + C(J,\kappa) \cdot (\Delta\theta_z^{x,y})] \cdot E, \end{aligned} \quad (16)$$

where J refers to the ground state J and $\Delta\theta_z^{x,y}$ is the change in Watson's coefficient upon vibrational excitation.

Table III lists $\delta\omega/E$ for the three observed transitions in SiH₄. From a weighted least-squares fit, we determined P to be $1.46(5) \times 10^{-2}$ D and $\theta_{z,4}^{x,y} = 2.97(19) \times 10^{-5}$ D. This corresponds to a variation in $\theta_z^{x,y}$ of $0.37(19) \times 10^{-5}$ D from the ground state value of $3.34(4) \times 10^{-5}$ D determined by Kagann, Ozier, and Gerry.²⁷ We observed therefore a change of roughly 11% which is rather larger than expected.

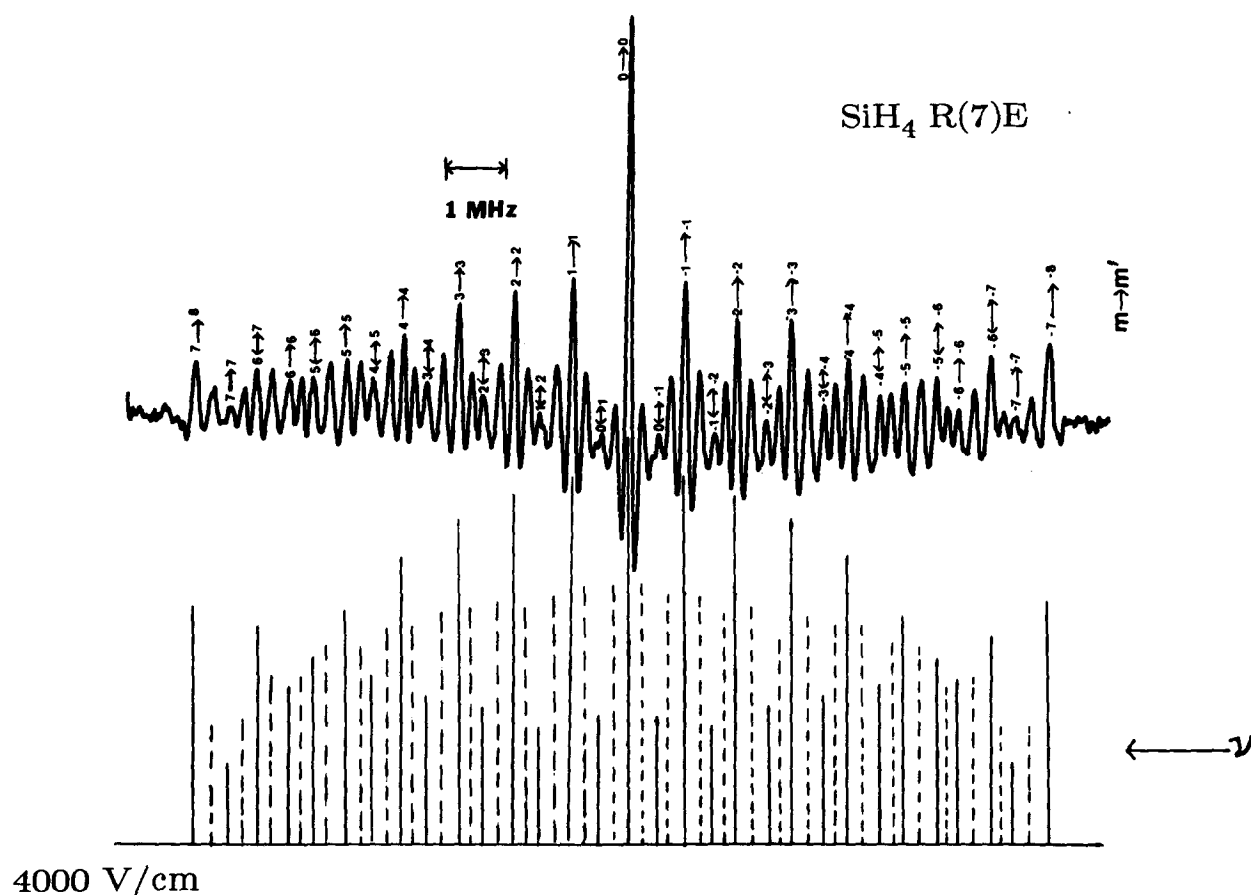
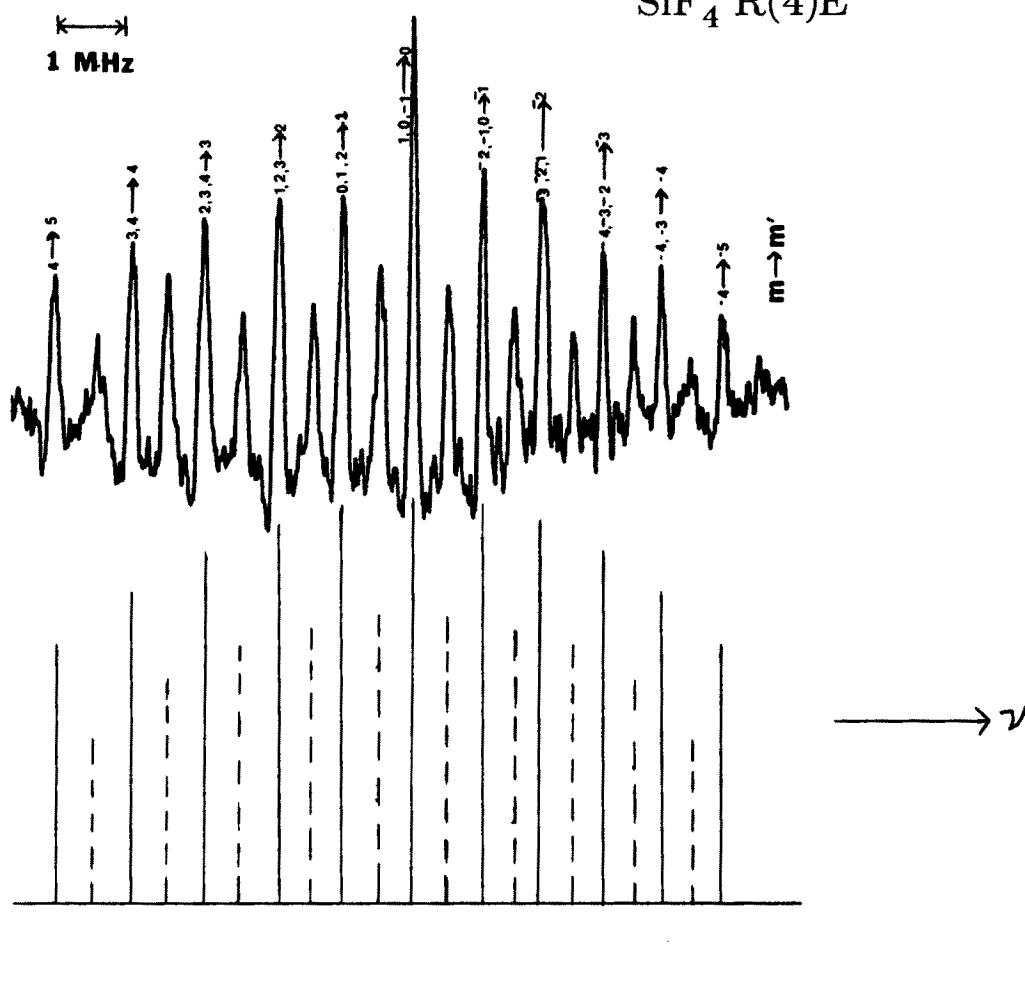


FIG. 3. The $\nu_4 \leftarrow 0 R(7)E$ transition of SiH₄, with a Stark field of 4000 V/cm, including assignments and calculated intensities. Solid lines correspond to normal Lamb dips; dashed lines correspond to center dips. Time constant is 300 ms and scan time is ~ 9 min.

SiF₄ R(4)E

1200 V/cm

FIG. 4. The $\nu_3 \rightarrow 0$ R(4)E transition of SiF₄ with a Stark field of 1200 V/cm, including assignments and calculated intensities. Solid lines correspond to normal Lamb dips; dashed lines correspond to center dips. Time constant is 300 ms and scan time is ~ 9 min.

V. CONCLUSIONS

We have determined the vibration-induced permanent dipole moments in SiH₄ and in SiF₄. An order of magnitude calculation suggests that P is smaller than a typical permanent dipole moment by a factor of κ^2 , where κ is the Born-Oppenheimer constant; these results confirm this. We have also determined Watson's coefficient for the centrifugal distortion-induced dipole moment in the excited vibrational state of SiH₄.

The higher value of P for SiF₄ is reasonable, because the bond dipole moment, related to the difference in electronegativity, is roughly nine times larger for Si-F than for Si-H which overcompensates for the smaller amplitudes of the SiF₄ vibration.

Further work on both of these molecules, especially SiH₄ should be directed towards observing more transitions. Unfortunately, only three transitions in the ν_4 band overlap with the ¹²C¹⁸O₂ sidebands. Additional lines could be stud-

TABLE II. Observed transitions in the ν_4 fundamental band of SiH₄.

Transition	Center frequency (THz)	Sideband	$\delta\omega/E^a$ (MHz/V/cm) ($\times 10^4$)
R(7)E	27.893 809 1(56)	10P(34) - 16 911.7	4.816(190)
R(8)E ⁽²⁾	27.954 732 2(25)	10P(32) - 14 717.6	- 3.862(56)
R(14)E ⁽³⁾	28.320 294 9(87)	10P(20) + 14 070.0	- 3.762(124)

$$P = 1.46(5) \times 10^{-2} \text{ D}$$

$$\theta_z^{\nu_4}(v_4 = 1) = 2.97(19) \times 10^{-5} \text{ D}$$

^a Separation between two subsequent $\Delta M = 0$ lines, divided by the magnitude of the electric field. A positive (negative) sign denotes that as frequency increases, M increases (decreases).

TABLE III. Observed transitions in the ν_3 fundamental band of SiF₄.

Transition	Center frequency (THz)	Sideband	$ E $ dc V/cm	Stark splitting ^a (MHz)
$P(11)E^{(1)}$	30.877 471 0(28)	$9P(38) + 15 573.5$	800	5.162
			1200	7.684(48)
			1600	9.936(90)
			2000	12.494(31)
			2500	15.811(82)
$P(11)E^{(2)}$	30.877 172 7(5)	$9P(38) + 15 275.2$	700	12.933(846)
$R(4)E$	30.939 458 3(29)	$9P(36) + 16 542.9$	1000	8.112(63)
$R(12)E^{(2)}$	30.968 885 6(72)	$9P(34) - 14 305.1$	2000	10.092(122)
			2100	10.831(59)
			2200	11.147(188)

$$P = 4.21(12) \times 10^{-2} \text{ D}$$

^a Defined as the separation between $M = J$ and $M = -J$ peaks, where M and J refer to the upper state quantum numbers.

ied using other isotopic species of CO₂. Additionally, the ν_2 band is in this region. Intensities are very low, but are observable due to ν_2 - ν_4 mixing. Although the ν_2 band is doubly degenerate and should not exhibit a vibration-induced dipole moment, this same mixing should generate a small vibration-induced Stark effect and it would be interesting to observe this.

Finally, as mentioned earlier, P is related to the cubic anharmonic force constants and the second derivative of the dipole moment. This determination can be used as an excellent check for these parameters and the theory. As of yet, they have not been calculated, although some overtone spectroscopy of SiF₄ has been reported.²⁸

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- ¹M. Mizushima, and P. Venkateswarlu, *J. Chem. Phys.* **21**, 705 (1953).
- ²I. M. Mills, J. K. G. Watson, and W. L. Smith, *Mol. Phys.* **16**, 329 (1969).
- ³K. Uehara, K. Sakurai, and K. Shimoda, *J. Phys. Soc. Jpn.* **26**, 1018 (1969).
- ⁴A. C. Luntz, and R. G. Brewer, *J. Chem. Phys.* **54**, 3641 (1971).
- ⁵M. Takami, *J. Mol. Spectrosc.* **93**, 250 (1982).
- ⁶R. F. Curl, and T. Oka, *J. Chem. Phys.* **58**, 4908 (1973).
- ⁷M. Takami, K. Uehara, and K. Shimoda, *J. Appl. Phys.* **12**, 924 (1973).
- ⁸I. Ozier, and A. Rosenberg, *J. Chem. Phys.* **69**, 5203 (1978).
- ⁹M. Takami, *J. Chem. Phys.* **73**, 2665 (1980).
- ¹⁰M. Takami, *J. Chem. Phys.* **74**, 4276 (1981).
- ¹¹M. Takami, *J. Chem. Phys.* **76**, 1670 (1982).
- ¹²A. A. Muentner, T. R. Dyke, W. E. Falconer, and W. Klemperer, *J. Chem. Phys.* **63**, 1231 (1975).
- ¹³A. C. Luntz, *Chem. Phys. Lett.* **11**, 186 (1971).
- ¹⁴J. K. G. Watson, *J. Mol. Spectrosc.* **50**, 281 (1974).
- ¹⁵W. E. Lamb, *Phys. Rev. A* **134**, 1429 (1964).
- ¹⁶R. G. Brewer, M. J. Kelley, and A. Javan, *Phys. Rev. Lett.* **23**, 559 (1969).
- ¹⁷G. Magerl, J. M. Frye, W. A. Kreiner, and T. Oka, *Appl. Phys. Lett.* **42**, 656 (1983).
- ¹⁸Y.-T. Chen, J. M. Frye, and T. Oka, *J. Opt. Soc. Am. B* **3**, 935 (1986).
- ¹⁹C. W. Patterson, R. S. McDowell, N. G. Nereson, B. J. Krohn, J. S. Wells, and F. R. Peterson, *J. Mol. Spectrosc.* **91**, 416 (1982).
- ²⁰J. W. C. Johns, W. A. Kreiner, and J. Susskind, *J. Mol. Spectrosc.* **60**, 400 (1976).
- ²¹G. Pierre, A. Valentin, and L. Henry (private communication).
- ²²K. T. Hecht, *J. Mol. Spectrosc.* **5**, 355 (1960).
- ²³A. J. Dorney and J. K. G. Watson, *J. Mol. Spectrosc.* **42**, 135 (1972).
- ²⁴H. A. Jahn, *Proc. Roy. Soc. London Ser. A* **168**, 469 (1938).
- ²⁵E. E. Uzgiris, J. L. Hall, and R. L. Barger, *Phys. Rev. Lett.* **26**, 289 (1971).
- ²⁶C. Freed, L. C. Bradley, and R. G. O'Donnell, *IEEE J. Quant. Electron.* **16**, 1195 (1980).
- ²⁷R. H. Kagann, I. Ozier, and M. C. L. Gerry, *J. Chem. Phys.* **64**, 3487 (1976).
- ²⁸C. W. Patterson and A. S. Pine, *J. Mol. Spectrosc.* **96**, 404 (1982).